EFFECT OF LOW-ENERGY OXYGEN PLASMA TREATMENT ON PHOTOLUMINESCENCE OF CARBON-BEARING POROUS ALUMINA

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In this study the effect of low-energy oxygen plasma treatment on the photoluminescence properties of the carbon-bearing porous alumina obtained in 0.4 M aqueous solution of tartaric acid at constant current density of 150 and 700 A m^{-2} was investigated. It was also established that in as-anodized samples carbon content is increased from 2.98 to 3.18 (wt.) % with increasing anodizing current density. Increase in current density from 150 to 700 A m^{-2} results only in decrease in photoluminescence intensity. Oxygen plasma treatment is shown not to change the character of the photoluminescence of the different samples, but results in the decrease in the intensity of photoluminescence in 1.2 and 2.2 times for porous alumina formed at 150 and 700 A m^{-2}, respectively. The impact of the oxygen plasma treatment was also observed on the photoluminescence transients. It was found that in the case of the samples formed at 150 A m^{-2} the average life-time of the centers was decreased from 1.78 to 1.76 ns and from 1.78 to 1.50 ns for ones formed at 700 A m^{-2}. It is associated with the oxidation of amorphous carbon embedded in porous anodic alumina due to chemical reaction with O_2 plasma.

Introduction

Composite carbon/anodic alumina materials have shown improved mechanical and electrical properties, which make them useful for sensing, catalyst, and battery applications [1]. Porous alumina formed in the aqueous solutions of organic acids is known to contain different carbon-bearing components, in particular amorphous carbon embedded into the anodic alumina by different functional groups, i.e. carboxyl, carbonyl, and hydroxyl [2]. These carbon-bearing components were shown to determine physical chemical and optical properties of porous alumina [3-5]. The plasma treatment was regarded as a promising technique to modify the surface chemical properties of the materials containing carbon [6]. So we aimed to study the effect of low-energy oxygen plasma treatment on the photoluminescence (PL) of the carbon-bearing porous anodic alumina formed in the aqueous solution of tartaric acid.

Methods

The carbon-bearing porous alumina was obtained by the double-sided anodizing of aluminum foil (99.99 % purity, 100 μm, AlfaAesar) in 0.4 M solution of tartaric acid at the constant current density of 150 and 700 A m^{-2} and temperature of (18.0 ± 0.1) °C during 40 min up to the complete oxidation of aluminum; at the stage of the oxide steady-state growth anodizing voltage was 200 V. The low-energy oxygen plasma treatment of the surface of samples was carried out by Leica EM SCD050 at 50 mA for 600 s. Carbon content was determined by Carbon/Sulfur analyzer ELATRA CS-2000. The top view of the porous alumina was studied by scanning electron microscope Zeiss DSM 982.

PL and time-resolved PL spectra were measured using Edinburg Instruments Fluorescence Spectrometer F900. Semiconductor diode laser EPL–375 emitting at 375 nm was utilized in the measurements.

Results and discussion

Carbon-bearing porous alumina samples formed in 0.4 M aqueous solution of tartaric acid at constant current density of 150 and 700 A m^{-2} have ordered porous structure with the pore diameter of 100-110 nm and the interpore distance of 400-440 nm (Fig. 1). As one can see, with increasing anodizing current the regularity of the porous structure is increased. There are no undeveloped pores in the sample obtained at J_{anod} = 700 A m^{-2}. It indicates that at high J_{anod} all pores are formed at the first stages of process. The carbon content is increased from 2.98 to 3.18 (wt.) % with increasing anodizing current density from 150 to 700 A m^{-2}.

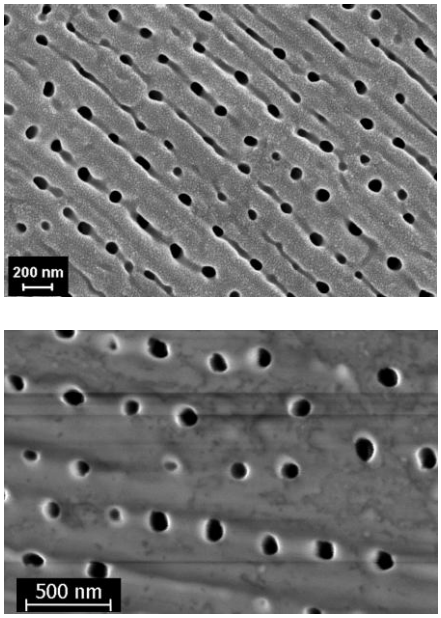

Fig. 1. SEM imaging of carbon-bearing porous alumina formed in 0.4 M aqueous solution of tartaric acid at constant current density of 150 (a) and 700 A m^{-2} (b).

The PL of the as-anodized and modified by O_2 plasma samples exhibit strong PL in the range of 400-700 nm with the maximum at 460-470 nm. Increase in J_{anod} from 150 to 700 A m^{-2} results in decrease in photoluminescence intensity in 3.3 times. As can be seen from the normalized to maximum

intensity PL spectra, oxygen plasma treatment does not change the character of the photoluminescence of the different samples, but results in the decrease in the intensity of photoluminescence in 1.2 and 2.2 times for porous alumina formed at 150 and 700 A m^{-2}, respectively (Fig. 2).

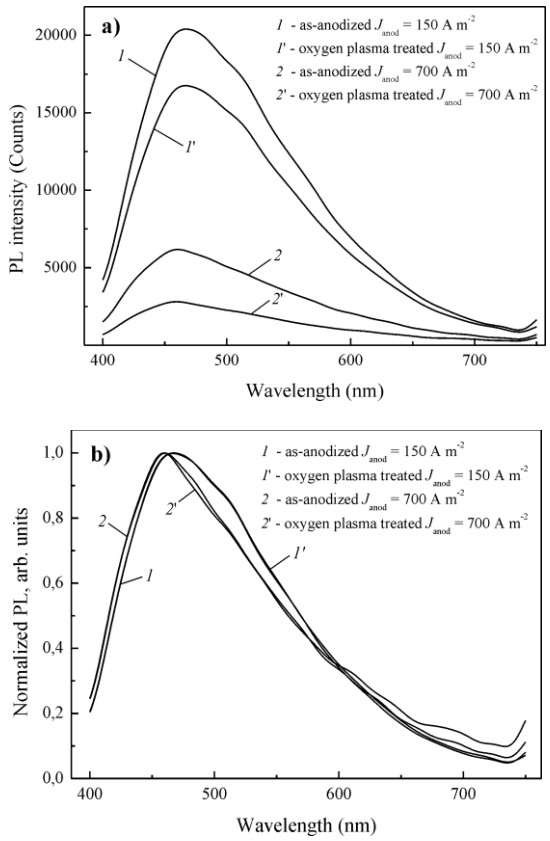

Fig. 2. PL (a) and normalized to maximum intensity PL (b) spectra of as-anodized and O_2 plasma treated carbon-bearing porous alumina formed at different current density, λ_{ex} = 375 nm.

The PL transients of the as-anodized and modified by O_2 plasma samples can be described by a three-exponential decay. Increasing J_{anod} does not result in the changes in the life-times of the PL centers. The average life-time of the centers was decreased from 1.78 to 1.76 ns in the case of the carbon-bearing porous alumina formed at 150 A m^{-2} and from 1.78 to 1.50 ns in the case of ones formed at 700 A m^{-2} (Table).

Table. The life-times for PL counterparts decay at PL peak 460 nm in as-anodized and O_2 plasma treated carbon-bearing porous alumina formed at different current density (λ_{ex} = 375 nm).

J_{anod}, A m^{-2}	τ_1, ns	τ_2, ns	τ_3, ns	τ_{av}, ns
As-anodized				
150	0.33	1.21	3.86	1.80
700	0.35	1.23	3.77	1.78
O_2 plasma treated				
150	0.32	1.17	3.80	1.76
700	0.17	0.83	3.51	1.50

It was shown that carbon-bearing porous alumina contains amorphous carbon with great amount of different functional groups, i.e. carboxyl, carbonyl, and hydroxyl; the formation of amorphous carbon during electrochemical oxidation of aluminium in the aqueous solution of tartaric acid is possible due to the consecutive reactions of dissociative adsorption, dehydration, decarboxylation, and dehydrocyclization tartaric ions [2-5]. The growing amount of embedded carbon and therefore of the growing disorder of the amorphous structure of the samples increases in the number of nonradiative recombination centres. This explained the decrease in the PL intensity with increasing current density and the unchanged character of the PL (see Fig. 2).

It is obvious that low-energy oxygen plasma not only cleans the surface of the samples but also chemically reacts with the surface of the carbon-bearing porous alumina. As is known, oxygen plasma treatment of the amorphous carbon results in the increase in the concentration of the carboxyl and carbonyl groups. The presence of carbon-related radicals in tartaric acid anodic alumina was established by electron paramagnetic spectroscopy [4, 7]. So, O_2 plasma modification of the carbon-bearing porous alumina causes the oxidation both of the carbon-related radicals and hydroxyl groups. The greater amount of carbon is in the samples the greater effect of O_2 plasma on the PL properties is observed (see Table).

Conclusion

By chemical semi-microanalysis it was established that carbon content is increased from 2.98 to 3.18 (wt.) % with increasing anodizing current density from 150 to 700 A m^{-2}, respectively. Increase in current density from 150 to 700 A m^{-2} results only in decrease in photoluminescence intensity. Oxygen plasma treatment is shown not to change the character of the photoluminescence of the different samples, but results in the decrease in the intensity of photoluminescence. It was also found that in the case of the samples formed at 150 A m^{-2} the average life-time of the centers was slightly decreased from 1.78 to 1.76 ns and from 1.78 to 1.50 ns for ones formed at 700 A m^{-2}. It is associated with the oxidation of amorphous carbon in porous anodic alumina due to chemical reaction with O_2 plasma.

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